Phase behavior in the reentrant-nematic region of chiral frustrated smectic liquid crystals

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A high-resolution ac calorimetric study has been carried out on two homologous polar liquid crystals with aromatic cores containing three phenyl groups and a flexible chiral linking group. The expected smectic polymorphism occurs, and there are several prominent thermal features in the nematic range between smectic-A_d and smectic-C phases. It is suggested on the basis of characteristic thermal signatures, helical pitch variations, and optical textures that a twist-grain-boundary phase and chiral line liquids (N*) exist as well as twisted nematic liquid crystals (N*~) with other kinds of short-range order. [S1063-651X(98)03607-1]

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I. INTRODUCTION

Smectic polymorphism and reentrant nematic phases are well known in “frustrated” smectic liquid crystals exhibiting long (three-ring) aromatic cores and a polar end group [1]. The best experimentally studied systems of this type are alkoxybenzoyloxy cyanostilbenes (T7 and T8) [2] and mixtures of alkoxyphenyl-nitrobenzoyloxy benzoates (DB8ONO2 + DB10ONO2) [3,4]. The theory of such systems has been developed along two different lines [5,6], both of which involve a competition between two length scales. One of these lengths is the molecular length L and the other is the polarization periodicity reflected in the layer spacing d for the partial bilayer smectic-A_d (SmA_d) phase (d ~ 1.2 L in the systems studied here).

It is also well known that chirality promotes twisted phases [7] such as the blue phases (BP’s), cholesteric (N*~), and twist-grain-boundary (TGB) phases. Theory has predicted both TGBA and TBGB phases [8–10]; the most extensive experimental studies of TGBA and TGBB are reported in Refs. [11, 12] and Refs. [13, 14], respectively.

Recently, studies have been carried out on the mesogenic phenyl butyrates R-(+)−4-[[(E)-2-(4-alkoxyphenyl)-1-diazene]-phenyl-3-(4-nitrophenyl)-butanoate, with the structural formula

\[
\text{C}_n\text{H}_{2n+1}\text{O} \begin{array}{c}
\text{N}(\text{O})\text{N} \\
\end{array} \begin{array}{c}
\text{OOC}−\text{CH}_2−\text{C}^*\text{H}(\text{CH}_3) \\
\end{array} \begin{array}{c}
\text{NO}_2 \\
\end{array}
\]

for homologs with \(n = 11−17\) [15,16]. This compound was denoted nAZY in Ref. [15], but we prefer the more structurally related abbreviation nOPBNO2 and will refer to it by this name. Since this polar compound contains a three-ring aromatic core with a chiral linking group, it should exhibit phase aspects of both frustrated smectics and chiral materials. The partial phase diagram shown in Fig. 1 exhibits the expected smectic polymorphism, and previous DSC studies of the \(n = 14−17\) homologs [16] indicated a prominent thermal feature in the nematic region, which was tentatively ascribed to a transition similar to the nematic \(N_d\)-nematic \(N_1\) transition reported in Ref. [17].

The present investigation involves a high-resolution ac calorimetric study of the R-enantiomers of 14OPBNO2 (\(M = 611.74\ \text{g mol}^{-1}\)) and 15OPBNO2 (\(M = 625.77\ \text{g mol}^{-1}\)), with special emphasis on the nematic region. One first-order transition and three non-transitional thermal features were observed in this region, as described in Sec. II. A discussion comparing the new results with those for systems with known TGB phases and proposing several N* regions with differing short-range order is given in Sec. III. It should be noted that the pitch in most of the nematic range for these \(n = 14\) and 15 compounds is found to be less than 0.2 \(\mu\)m (ultraviolet region), which indicates a substantial chirality (twisting tendency).

II. CALORIMETRIC AND OPTICAL RESULTS

The synthesis and purification of the investigated phenyl butyrates (as described in Ref. [15]), optical observations of textures and helical pitch, and DSC scans were carried out at the University of Warsaw. The heat capacity data given for the \(n = 14\) and 15 homologs in Figs. 2 and 3 were obtained at MIT with a high-resolution ac calorimeter, operated over a range of frequency from \(2\omega_0\) to \(\omega_0/8\), where \(\omega_0 = 2\pi f_0 = 0.196\ \text{s}^{-1}\). A small mass (~30 mg) of liquid crystal was cold-weld sealed into a thin silver cell, and the temperature was scanned slowly (0.1–0.2 K h^{-1}) to ensure thermody-
namic equilibrium for the mesogenic phases. No appreciable drift in the position of \( C_p \) peaks was observed over a period of eight weeks. The calorimeter and the equations for analyzing the observed \( T_{ac} \) response to the \( P_{ac} = P_0 \exp(i\omega t) \) heat input are described elsewhere \cite{18,19}. The 14OPBNO \(_2\) data in Fig. 2 were obtained at \( \omega_0/4 \approx 7.8 \) mHz and the 15OPBNO \(_2\) data in Fig. 3 at \( \omega_0/2 \). In both cases, these are static values in one-phase regions since \( C_p \) values obtained at lower frequencies agreed well with those shown.

Also displayed in Figs. 2 and 3 are insets indicating the typical anomalies in the imaginary component \( C_p^{\prime\prime} \), related to phase shifts \( \phi \) between \( T_{ac} \) and \( P_{ac} \) seen at first-order transitions where there is two-phase coexistence \cite{18,20}. In other regions, \( C_p^{\prime\prime} \) is essentially independent of \( T \) and very small (\( \approx 0.003 \) J K\(^{-1}\) g\(^{-1}\)) except for an unusual smooth rise in \( C_p^{\prime\prime} \) for 15OPBNO \(_2\) on cooling from \( \approx 338 \) K to the freezing point at 330.7 K. Over this \( \approx 7 \) K range, \( C_p^{\prime\prime} \) increases by 0.061 J K\(^{-1}\) g\(^{-1}\) (from \( \approx 0.006 \) to 0.067 J K\(^{-1}\) g\(^{-1}\)) for \( \omega_0/2 \). This effect is frequency dependent: the increase in \( C_p^{\prime\prime} \) is 0.115 J K\(^{-1}\) g\(^{-1}\) at 2 \( \omega_0 \) but disappears at \( \omega_0/6 \) and \( \omega_0/8 \). Thus, this \( C_p^{\prime\prime} \) effect is due to sluggish dynamics in this temperature region and not to two-phase coexistence \cite{19}.

The thermal features shown in Figs. 2 and 3 are listed in Table I together with melting temperatures of the crystal phase on heating and previously reported DSC values for the high-temperature isotropic (I)–smectic-A \(_d\) (Sm\(_{A_d}\)) transitions. Note that several of the transitions are monotropic since there is a considerable difference between the freezing and melting temperatures. In the case of 14OPBNO \(_2\), the sample was quenched to 330.5 K and a heating run was immediately begun prior to any freezing. This was not done....
TABLE I. Transition temperatures (K) and enthalpies (J g\(^{-1}\)) for chiral nOPBNO\(_2\). \(T_2 - T_6\) denote three nonsingular (rounded) \(C_p\) features that do not correspond to thermodynamic phase transitions. \(m\) denotes that the feature is monotropic.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Proposed structure</th>
<th>Proposed transition</th>
<th>Order</th>
<th>(n = 14)</th>
<th>(n = 15)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I)</td>
<td>(I)</td>
<td>(I)-Sm(A_{d})</td>
<td>1st</td>
<td>(T_{1}) [16]</td>
<td>(\sim 396)</td>
</tr>
<tr>
<td>Sm(A_{d})</td>
<td>Sm(A_{d})</td>
<td>Sm(A_{d})-N(_d^*)</td>
<td>1st</td>
<td>(T_{2})</td>
<td>359.68</td>
</tr>
<tr>
<td>(N_\alpha^*)</td>
<td>(N_\beta^*)</td>
<td>(N_\beta^<em>)-N(_d^</em>)</td>
<td>non</td>
<td>(T_{3})</td>
<td>?</td>
</tr>
<tr>
<td>(N_\beta^*)</td>
<td>(N_\gamma^*)</td>
<td>(N_\gamma^<em>)-N(_{LA}^</em>)</td>
<td>non</td>
<td>(T_{4})</td>
<td>344.55</td>
</tr>
<tr>
<td>(N_\beta^*)</td>
<td>(N_\gamma^*)</td>
<td>(N_\gamma^<em>)-N(_{LC}^</em>)</td>
<td>non</td>
<td>(T_{5})</td>
<td>340.57, (m)</td>
</tr>
<tr>
<td>(N_\alpha^*)</td>
<td>(TGB_{C})</td>
<td>TGB(_{C})-Sm(\tilde{C})</td>
<td>1st?</td>
<td>(T_{6})</td>
<td>331.22, (m)</td>
</tr>
<tr>
<td>Sm(\tilde{C})</td>
<td>Sm(\tilde{C})</td>
<td>freeze to K</td>
<td>1st</td>
<td>(T_{8})</td>
<td>330.35(^a)</td>
</tr>
<tr>
<td>K</td>
<td>K</td>
<td>K melt</td>
<td></td>
<td></td>
<td>344.05(^a)</td>
</tr>
</tbody>
</table>

\(^a\)TGB\(_{C}\) freezes into \(K\); \(K\) melts into N\(_{LA}^*\).

\(^b\)Sm\(\tilde{C}\) freezes into \(K\) at a scan-rate-dependent temperature; \(K\) melts into N\(_{LC}^*\).

for 15OPBNO\(_2\), and only cooling run data are available below 340 K. The symbols N\(_d^*\) to N\(_\alpha^*\) are used in Fig. 1 and Table I to denote the various twisted phases observed in the reentrant nematic region. The low-temperature smectic phase that we assign as Sm\(\tilde{C}\) is denoted as Sm\(X\) in Ref. [16], where on the basis of preliminary x-ray powder patterns it was shown to be either a weakly tilted Sm\(\tilde{C}\) phase or an incommensurate orthogonal smectic mesophase. A discussion of possible structures for N\(_d^*\)-N\(_\alpha^*\) in terms of twist-grain-boundary, chiral line liquids N\(_{LC}^*\), and twisted nematic N\(_*\) phases is given in Sec. III.

The first-order character of the transitions at \(T_2\) and \(T_6\) is very clear. In both compounds there are characteristic low-frequency \(C_p\) peaks that arise from ac phase-shift anomalies and indicate two-phase coexistence [20]. The width of the coexistence region at \(T_2\) is \(\sim 0.8\) K for \(n = 14\) and \(\sim 1.0\) K for \(n = 15\), while the coexistence width at \(T_6\) is \(0.35\) K for \(n = 14\) and \(0.23\) K for \(n = 15\). Furthermore, there is a substantial hysteresis of 0.5 K at the \(T_2\) transition for \(n = 15\). The \(T_6\) hysteresis is very small for the \(n = 14\) compound (0.01 K) and was not investigated for \(n = 15\). Estimated values of the latent heats \(\Delta H_2\) and \(\Delta H_6\) given in Table I are taken to be the total DSC enthalpies reported in Ref. [16] for these transitions.

The nature of the \(T_7\) thermal feature observed in 15OPBNO\(_2\) is uncertain. If it were found by structural studies to be a TGB\(_{C}\)-Sm\(\tilde{C}\) transition, one would expect it to be first order like the analogous TGB\(_{C}\)-Sm\(C^*\) transition [14]. However, in the latter case the variation of \(C_p(ac)\) is very small and the latent effect associated with this transition is observed only by nonadiabatic scanning calorimetry, which was not used in the present study. Both the \(C_p(ac)\) and the new DSC runs show a rounded \(T_7\) feature for 15OPBNO\(_2\), and there are no obvious anomalies in the phase shift \(\phi\) signifying two-phase coexistence at \(T_7\). However, such \(\phi\) anomalies are subtle at the TGB\(_{C}\)-Sm\(C^*\) transition [14]. We have tentatively assumed a first-order character and list the DSC area in Table I as the latent heat \(\Delta H_7\). This value of \(\sim 0.05\) J g\(^{-1}\) agrees well with latent heats of 0.052 and 0.126 J g\(^{-1}\) reported for two TGB\(_{C}\)-Sm\(C^*\) transitions [14]. Note that a “\(T_7\) transition” is missing for 14OPBNO\(_2\) due to the sample freezing just below \(T_6\).

The features labeled \(T_3\), \(T_4\), and \(T_5\) denote nontransitional evolutions of the short-range order in the nematic phase. These three features are obvious from rounded \(C_p\) peaks observed for 15OPBNO\(_2\), but the \(T_3\) feature is not obvious for 14OPBNO\(_2\) and the \(T_5\) feature is seen as a rounded step (see Fig. 2). None of the \(T_3\), \(T_4\), \(T_5\) features exhibit hysteresis, there are no \(C_p\) peaks or other anomalies associated with these features, and the shapes of the \(C_p\) peaks do not correspond to either first-order behavior or singular second-order behavior.

Although it is difficult to make a precise evaluation of the excess heat capacity \(\Delta C_p\) due to ambiguities in
other or from nontransitional thermal features. Such distinctions require high-resolution data obtained at slow scan rates.

An additional DSC study was undertaken on mixtures of chiral R-16OPBNO$_2$ and its racemate, and the resulting phase diagram is given in Fig. 4. As the chiral mole fraction $X_R$ is decreased, the $N_{a}^*$ and $N_{c}^*$ phases disappear and the phase sequence becomes SmA$_d$-$N_{a}^*$-$N_{c}^*$-$N_{b}^*$-$SmC$ at $X_R = 0.8$. Note that the location of the $T_4$ line is uncertain since DSC scans of mixtures do not resolve the small $T_4$ feature on the low-temperature side of an asymmetric $T_2$ peak. As the chirality is further reduced, the remaining $N_{a}^*$ phase regions decrease and disappear and a SmC$_d^*$ tilted bilayer phase appears. The DSC enthalpy for the combined $T_4+T_5$ features decreases from 0.45 J g$^{-1}$ at $X_R = 0.9$ to 0.07 J g$^{-1}$ at $X_R = 0.7$.

Optical measurements made at Warsaw University show that the helical pitch for the $n$=14 and 15 homologs in the $N_{a}^*$, $N_{c}^*$, and $N_{b}^*$ phases is less than 0.2 μm. As the temperature approaches the SmA$_d$ and SmC$_d$ boundaries, the helical pitch increases rapidly ($|dP/dT|$~0.13 μm/K) to give selective light reflections in the visible. Such a small pitch in reentrant $N_{a}^{*}$-$N_{c}^{*}$ nematic phases confirms the substantial chirality of these compounds. Also the width of the region of rapid increase in pitch on heating 15OPBNO$_2$ near the SmA$_d$ boundary is 1.0 K, which exactly agrees with the width of the calorimetric region labeled $N_{a}^*$, and the width of the region of rapid increase of pitch on cooling near the SmC$_d$ boundary is 0.75–1.7 K, which compares well to the $N_{a}^*$ range of 1.36 K from calorimetry.

In the nematic region from $T_3$ to $T_6$, where Fig. 1 indicates the presence of $N_{b}^*$, $N_{c}^*$, and $N_{a}^*$, smooth optical textures with a few oily streaks were observed, which are typical for chiral nematics with small helical pitch values. However, when the sample was heated or cooled rapidly, small square defects appeared in the $N_{a}^*$ temperature range between $T_4$ and $T_5$. These may be due to parabolic defects induced by small discontinuities in the helical pitch. At temperatures above $T_2$ and below $T_7$, fan textures were observed. In a freely suspended film (which should align the smectic layers parallel to the film surface), the SmA$_d$ phase yielded a uniform homeotropic texture. The uniaxial untitled character of the SmA$_d$ phase was also confirmed by conoscopic figures. In a freely suspended film of the low-temperature SmC$_d$ phase, a uniform homeotropic texture was never observed and a weak fan texture was seen.

### III. DISCUSSION

For the chiral $n$OPBNO$_2$ homologous series, the observed phase sequence is SmA$_{d}$-$N_{a}^{*}$-BP's-I for $n=\leq12$ and SmA$_{d}$-$N_{c}^{*}$-SmA$_{d}$-$N_{a}^{*}$-BP's-I for $n=13$, whereas the sequence is SmC (=SmX)-$N_{a}^{*}$-SmA$_{d}$-I for $n=14–16$ [16]. Such smectic phase behavior is typical for long-core frustrated smectic liquid crystals with rigid linking groups between the phenyl rings [1–6] and occurs here where nOPBNO$_2$ has a flexible chiral linking group in the core. The discussion below will focus on the thermal behavior in the nematic region and will provide qualitative arguments in support of the structures proposed for the five phases.

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** FIG. 4.** Phase diagram for mixtures of R-16OPBNO$_2$ and its racemate obtained from DSC scans made at 1 K min$^{-1}$. $X_R$ is the mole fraction of the chiral enantiomer.

$C_p$(background), an estimate has been made of the excess enthalpy $\delta H$ associated with the combined $T_4$ and $T_5$ features using

$$\delta H = \int \Delta C_p dT,$$

where the excess heat capacity is $C_p = C_p$(observed) $- C_p$(background). The $C_p$(background) values are indicated by the dashed lines in Figs. 2 and 3. The choice of $C_p$(background) is especially difficult for 16OPBNO$_2$ since the first-order $T_6$ transition is much closer to $T_4$ (~6.3 K compared to ~13.3 K for 14OPBNO$_2$). The resulting enthalpies $\delta H$ are 0.65 J g$^{-1}$ for 14OPBNO$_2$ and 0.61 J g$^{-1}$ as an estimated lower bound for 15OPBNO$_2$.

DSC scans carried out at Warsaw University confirm qualitatively most of the thermal features obtained with ac calorimetry. For the $n=15$ and 16 compounds, better DSC resolution was obtained than that shown in Ref. [16] and six peaks corresponding to $T_3$–$T_7$ were observed above the freezing temperature. For the $n=14$ compound, DSC and ac calorimetry agree in that neither shows a peak at $T_3$ and both show freezing occurs just below $T_6$ (even at a DSC scan rate of 5 K/min). The DSC for $n=14$ does not show the step feature in $C_p$ at $T_5$. DSC transition temperatures obtained on heating are systematically 1.1 K higher than those determined with ac calorimetry, due in part to rapid DSC scan rates and in part to absolute temperature calibrations. The $n=16$ points in Fig. 1 have been shifted by 1.1 K to permit a better correspondence with the present data for $n=14$ and 15. It should be noted that DSC scans do not allow one to distinguish first-order and second-order transitions from each other.
The most likely assignments for these phases are TGB$_A$ or TGB$_C$ (twist-grain-boundary phases with SmC or Sm$ar{C}$ blocks) for $N^*_a$, $N^*_a$ with short-range TGB$_C$ order for $N^*_a$, $N^*_a$ (chiral line liquid with short-range TGB$_A$ order) for $N^*_d$, cholesteric $N^*_d$ (twisted nematic with weak smectic fluctuations) for $N^*_d$, and $N^*_d$ (a weakly twisted nematic with dominant short-range Sm$_{Ad}$ fluctuations) for $N^*_d$. These proposed assignments are summarized in Table I. High-resolution x-ray studies on aligned single domain samples are needed to verify the presence of such TGB and chiral line liquid structures.

Based on the assignments proposed above, the transition at $T_d$ corresponds to SmA$_d$-N$_d^*$. Where the nematic phase $N^*_d$ is a long-pitch cholesteric with substantial short-range Sm$_{Ad}$ fluctuations, which are expected to decrease and change in character on further cooling [21]. An example where such reentrant N$_d$ behavior is established in analogous nonchiral frustrated smectic liquid crystals is given for octlyoxybenzoyloxy cyanostilbene (T8) in Ref. [2]. However, the presence of an asymmetric chiral center inside the aromatic core should strongly promote twisting, and the SmA$_d$ fluctuations are in competition with this twisting tendency. Thus one expects $N^*_d$ to evolve into $N^*_d$, which has a short pitch and weak smectic fluctuations. We assign this nontransitional change in nematic character to the thermal feature at $T_3$ in 15OPBNO$_2$ and the associated significant change in pitch variation $|dP/dT|$. No thermal $T_3$ feature is visible in 14OPBNO$_2$, but this is consistent with the smooth evolution of short-range Sm$_{Ad}$ character to short-range SmC character in the nematic phase of T8 with only a single $C_p$ peak [2]. In the present materials, the asymmetry of the $C_p$ peak associated with the first-order transition at $T_d$ is different from the usual shape of second-order $N$-Sm$_{Ad}$ peaks. However, similar asymmetry (large $N^*_d$ pre-transitional wing and small Sm$_{Ad}$ wing) has also been observed in mixtures of octlycyanobiphenyl (8CB) and a chiral compound [22], where it is ascribed to energy effects related to the development (or expulsion) of the cholesteric twist.

The most prominent $C_p$ feature in the nematic region is the broad rounded peak at $T_4$. This has been assigned to the nontransitional development of short-range TGB$_C$ character to create a chiral line liquid $N^*_d$. Such a chiral line liquid has been predicted theoretically [10] as the liquid crystal analog of the Abrikosov flux vortex liquid in type-II superconductors. Since $N^*_d$ and $N^*_d$ have the same macroscopic symmetry, no thermodynamic transition should occur, and this is verified experimentally. Indeed, a large rounded $C_p$ peak is a striking characteristic of the evolution of $N^*_d$ into a chiral line liquid [12,14]. Furthermore, the $C_p$ feature at $T_4$ does not correspond to behavior like that observed for $N_d$-$N_d$ transitions in nonchiral systems where the smectic fluctuations change from SmA$_d$-like to SmA$_1$-like [17]. It should also be noted that racemic 14OPBNO$_2$ and 15OPBNO$_2$ samples do not exhibit an analogous $T_d$ thermal feature in their reentrant $N$ phases. Furthermore, the character of the small texture changes reported near $T_d$ in the chiral homologs [16] supports this assignment as a change in the short-range order. Thus the evidence for the appearance of a chiral line liquid at $T_d$ is indirect but very strong.

We suggest that the smectic blocks in the $N^*_d$ chiral line liquid may have SmA character and use the symbol $N^*_d$ to indicate this assignment. The thermal feature at $T_3$ is also experimentally shown to be a nontransition—no first-order coexistence or latent heat but $C_p(T)$ is not singular as it would be at a second-order transition. We suggest this feature may be due to a change in the character (tilt) of the smectic blocks that make up the short-range TGB order: $N^*_d$-$N^*_d$. The presence of short-range smectic-C order is supported by the presence of a stable SmC$_d$ phase in Fig. 4 and in racemic 15OPBNO$_2$ [16].

The observed rapid increase in pitch on cooling both 14OPBNO$_2$ and 15OPBNO$_2$ below $T_6$ corresponds very well with previously observed pitch variations in the TGB$_C$ phase [13], and the first-order transition at $T_6$ is assigned as $N^*_d$-TGB$_C$. This is analogous to the established $N^*_d$-TGB$_C$ transition in chiral compounds with a SmC$^*$ phase [14]. We are assuming that parallel behavior can occur where the underlying smectic phase in SmC$^*$ rather than SmC*. However, in view of the very small $\Delta H_f$ latent heat associated with the TGB$_C$-SmC transition in 15OPBNO$_2$, the structure of the TGB$_C$ phase must be very similar to that of the SmC$^*$ phase. Thus it might be possible that this is a new TGB$_C$ phase where the smectic blocks have SmC$^*$ structure. The argument against this is that such a structure would require grain boundaries with two types of more or less orthogonal dislocations, and the stability of these complex grain boundaries would be poor [23].

It is appropriate to mention two other possible phase sequences: (1) SmC$^*$-TGB$_C$-TGB$_A$-$N^*_d$-$N^*_d$-$N^*_d$-SmA$_d$ or (2) SmC$^*$-TGB$_{C_1}$-TGB$_{C_2}$-$N^*_d$-$N^*_d$-$N^*_d$-SmA$_d$ where there are two different TGB$_C$ phases. There is theoretical [8,9] and experimental [11,13,14,24] support for each of these sequences. However, if the transition at $T_3$ were to correspond to a $N^*_d$-TGB$_C$ transition it should be first order [12,14], whereas the present data show that the $T_3$ heat capacity peaks are nontransitional features. Furthermore, in the second case one would expect a rapidly varying and large pitch in both TGB$_C$ phases [24], whereas we see a rapid increase in pitch on cooling only over a narrow temperature range corresponding to the single $N^*_d$ region shown in Fig. 1.

It is useful to compare the widths and integrated enthalpies for the combined $T_d$ and $T_4$ peaks with published values for $N^*_d$-$N^*_d$ in TGB$_A$ materials and $N^*_d$-$N^*_d$ in TGB$_C$ materials. The “width” is ~15 K and $\delta H = 0.65$ J g$^{-1}$ for 14OPBNO$_2$, and these values are ~10 K and 0.6 J g$^{-1}$ for 15OPBNO$_2$. For $N^*_d$-$N^*_d$, the widths range from 5 to 11 K and $\delta H$ values vary from 0.8 to 1.8 J g$^{-1}$ [12,14]. For $N^*_d$-$N^*_d$, the respective values are 5-8 K and 0.28-0.7 J g$^{-1}$ [14]. Thus the substantial amount of short-range ordering that occurs over a wide temperature range is comparable in all three cases. The latent heats of 0.14 and 0.3 J g$^{-1}$ for two $N^*_d$-TGB$_C$ transitions reported in Ref. [14] also correspond very well with the DSC latent heat estimates for the transitions at $T_d$ that we ascribe to $N^*_d$-TGB$_C$ (see Table I). It has already been pointed out in Sec. II that the TGB$_C$-SmC$^*$ $\Delta H_f$ latent heat of ~0.05 J g$^{-1}$ is comparable to TGB$_C$-SmC$^*$ values [14].

Evidence about the structure of the low-temperature...
smectic-X phase for compounds with n \geq 14 is limited in Ref. [16] since it is based on the x-ray powder pattern of the n = 16 compound at a single temperature plus microscopic textures as a function of temperature for several homologs. Our assignment of this phase as SmC is largely by analogy with the phase behavior of nonchiral frustrated smectics [3,4]. Note that a SmC phase can exhibit weak molecular tilt; see Ref. [4] and Fig. 10 in Ref. [3]. Clearly a high-resolution x-ray study is needed to confirm our SmC assignment and to establish the structures of the TGB_C and N_{LC} phases. However, it should be pointed out that the microscopic textures in the SmX phase of Ref. [16] are typical of the SmC textures reported in Ref. [25]. Moreover, recent x-ray studies of the n = 16 compound as a function of temperature [26] show that in the temperature range corresponding to the SmC phase there are two Bragg reflections at 2q_0 and q' < 2q_0. The q'' = 2q_0 - q' peak expected for SmC should be at a small angle (less than 1°) and thus difficult to resolve with the low-resolution Siemens area detector system used in this work. Two relatively strong diffuse x-ray reflections were also observed in the reentrant nematic phase. Their growth in intensity on approaching the SmC phase indicates the existence of SmC-like fluctuations in the low-temperature end of the nematic phase (the TGB_C region). Thus, all the currently available information is consistent with our assignment of SmX as SmC.

A final comment should be made about the overall increase in C_p on cooling 15OPBNO_2 between T_3 and T_8. In this case, the background slope dC_p/dT is negative (roughly -4 \times 10^{-3} J K^{-2} g^{-1}) rather than positive like 14OPBNO_2, (approximately +6.3 \times 10^{-3}) or the TGB_C systems in Ref. [14] (approximately +3.0 \times 10^{-3}). The results in Figs. 2 and 3 were reproducible on several runs taken on two different samples of each compound, but we have no definite explanation of this different 15OPBNO_2 behavior. As noted in Sec. II, there are sluggish dynamics below 338 K for 15OPBNO_2 suggesting long-range effects. We speculate that this feature might be due to a pretransitional rise in C_p associated with a transition that is preempted by freezing. For example, the SmC-SmC transition in DB_4ONO_2 +DB_4ONO_2 mixtures exhibits a large inverted Landau C_p peak with the SmC heat capacity showing an increase on cooling starting \approx 10 K above the transition [3]. A similar pretransitional increase in the smectic heat capacity also occurs in butyloxybenzidene octanol (4O.8) above the SmC-plastic CrB transition [27]. In the case of 14OPBNO_2, freezing preempts the SmC phase so this feature is not seen.

In summary, the competition between chiral twist and long-core frustrated smectic length scales gives rise to an interesting and rich phase behavior. One first-order transition and several nontransitional thermal features have been established in the nematic phase of 14OPBNO_2 and 15OPBNO_2. A variety of indirect evidence has been presented for the existence of a TGB phase and chiral line liquids N^*_L as well as two types of N^*_g twisted nematic phases. A high-resolution x-ray study of well-aligned samples is needed to confirm the proposed phase structures.

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[21] Although a SmC* phase has been reported in [16] to exist in a narrow temperature range below the SmA phase for the chiral n = 17 homolog, the thermal behavior at T_2 as well as the optical texture and pitch variation between T_2 and T_3 indicate that the N* phase cannot be SmC*.

[22] G. S. Iannacchione, S. Qian, M. Wittebrood, and D. Finotello, Mol. Cryst. Liq. Cryst. 302, 989 (1997); the asymmetry was most apparent for mixtures with higher amounts (11–13%) of chiral component than those shown in this paper.

[23] T. C. Lubensky (private communication).


